Closed-Loop Control of Laser Surface Treatment via Laser Induced Breakdown Spectroscopy

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Abstract: *Current composite manufacturing rates need to be improved to meet the projected demand of on-demand mobility (ODM) and commercial aircraft transports. Some processes in the composite manufacturing chain require touch labor such as manual sanding of surfaces prior to bonding and installing thousands of mechanical fasteners in bonded primary structures to achieve Federal Aviation Administration (FAA) certification. The consequences are insufficient repeatability in bond quality resulting in increased manufacturing time. The FAA has indicated that robust process control is one potential means of certifying bondlines in primary structure. This work describes an integrated closed-loop control system between a laser machining system and laser induced breakdown spectroscopy (LIBS) instrumentation as a means of assuring bond performance and achieving certified composite bondlines. Preliminary results from in-situ treatment and inspection are presented. Results indicate that LIBS inspection and laser treatment can be conducted simultaneously to achieve high quality, reliable adhesive bonds.*

Keywords: LIBS; laser ablation; automation; composite manufacturing; adhesive bonding

1. Introduction

Laser ablation is the removal of material by laser irradiation through photochemical, photothermal, or photophysical mechanisms, which is useful for preparation of an adherend surface for adhesive bonding. Laser surface treatment is a method that has been under research for the past decade at the NASA Langley Research Center (LaRC) to prepare aerospace materials [1-4] for adhesive joining. Laser ablation of composite materials removes the surface contaminants introduced during material handling and fabrication processes. The adjustment of laser parameters enables repeatable surface conditions, and superficial contaminants can be selectively and efficiently removed without damaging the underlying carbon fibers or the carbon fiber reinforced polymer (CFRP) structure [1-3].

At NASA LaRC, a single laser system has been used for both laser surface treatment and laser induced breakdown spectroscopy (LIBS), which enables in-situ monitoring of surface contaminants. The main contamination agent that has been investigated is silicone, which is ubiquitous in composites fabrication processes and, even at minute concentrations, can drastically decrease the performance of adhesive bonded structures. The complete removal and verification of removal of this contaminant is critical for the durability and performance of bonded parts. Silicones can be monitored using the silicon peak from the LIBS data. The silicon peak and carbon peak (mainly from the CFRP material) are used to determine the silicon to carbon ratio, Si/C, as an analytical parameter to quantify the silicone concentration.

This work describes the integration of a laser machining system and LIBS instrumentation to enable closed-loop control. The closed-loop control mechanism will ensure that treated surfaces meet quality criteria prior to adhesive bonding. The main goal for this integrated system is assuring bond performance and achieving certified composite bondlines.

2. Laser induced breakdown spectroscopy

LIBS is a characterization technique that utilizes an intense laser source to excite a target material into a plasma state, and upon relaxation, the chemical species emit light, which provides information about the elemental composition. When LIBS uses short/ultrashort pulse widths (e.g., hundreds of ps to 10 fs), there is a short exposure of the material to the light irradiation and minimal heat transfer, thus, reducing the oxidation effects [5]. For polymers, when the laser intensity irradiated on the material is sufficient, mechanical stress is induced by multiphoton transition. If the mechanical stress is sufficient, it produces bond dissociation, and the material is removed from the target surface by fragmentation [6,7]. There is minimal energy transferred to the regions outside the irradiated material volume, thus, producing less thermal stress in the material [8].

A typical LIBS apparatus (Figure 1) is comprised of a laser source and a spectrometer, which includes a detector, e.g., charge-coupled device (CCD) array, and a spectrograph. The laser beam is usually focused to enhance spatial resolution and to deliver maximum laser intensity irradiation on the target surface.

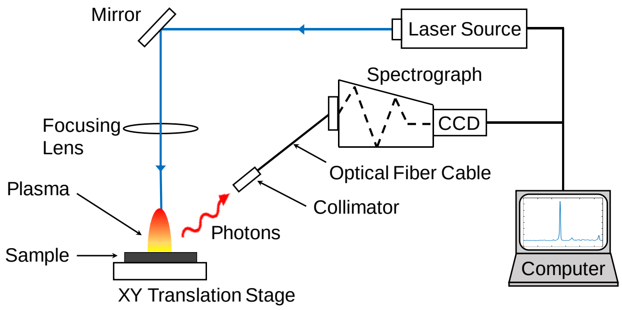

Figure 1. Typical LIBS apparatus comprised of a laser source, a spectrograph, a CCD-based detector, and a computer for data acquisition and laser control.

Significant advantages of LIBS measurements are that they can be conducted in open air and without sample preparation, and the results can be obtained near-instantaneously or in real-time. Advancement in the LIBS technique has shown that it can match or exceed the surface sensitivity of X-ray photoelectron spectroscopy (XPS) [9].

3. Laser ablation

At NASA LaRC, the laser ablative surface treatment is commonly conducted with a 355 nm wavelength, 10 ps pulse width, high repetition rates between 300 and 400 kHz, scan speeds in the order of 25.4 cm/s, and average laser powers of hundreds of mW. These conditions produce many overlapping low-energy (usually < 2 μJ) laser pulses [10,11]. The overlapping of the pulses increases the ablated material. However, the laser parameters used for surface treatment differ from the ones for LIBS [8,10,11]. Current LIBS inspections are conducted using a single laser pulse on a fresh (untested) surface and low energy pulses of at least 15 μJ to improve surface

sensitivity and limit of detection [8], and to minimize the ablated material required to generate a LIBS spectrum for analysis. The laser treatment parameters are being investigated to enable simultaneous in-situ LIBS inspections.

4. Closed loop control system

At NASA LaRC, efforts are being made to enable feedback control by integrating the laser system and the LIBS system [12]. By enabling synchronous control, the automation of the laser ablation and the spectral data collection will allow repeatable and instantaneous surface inspection while the surfaces are being laser treated for adhesive bonding. The automation of the processes will improve the surface inspection and bonded structure certification times. Figure 2 shows the main components and processes of the closed loop control system. The LIBS control system is used to set up the LIBS parameters for data collection such as the gate width, gate delay and number of pulses. After data collection, the LIBS control system calculates the Si/C ratio, which is used as a decision parameter. The communication and command exchange between the proprietary laser control system and the LIBS control system is through the transmission control protocol (TCP). The laser control system is used for the setup of the laser parameters and the XY stage movement. After the LIBS control system triggers the laser operation, the LIBS process begins. Each pulse generated by the laser system will trigger the spectrometer to record the plasma plume emission. Once the spectra collection is finished, the data processing and Si/C ratio determination are conducted automatically to assess the surface quality and determine whether the laser ablation process is complete or further treatment is needed.

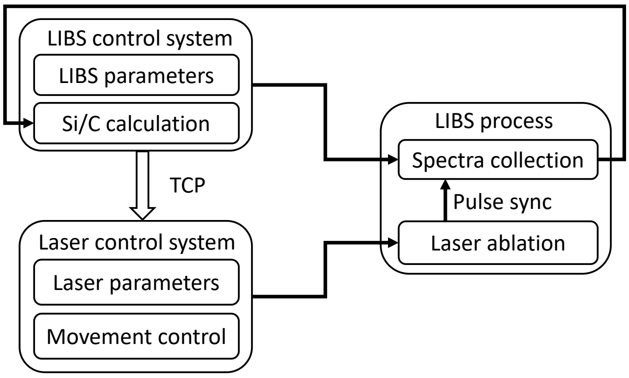

Figure 2. Diagram of the closed loop control system.

5. LIBS applications for CFRP

The applicability of LIBS has been documented [2,3,8,11]. The main focus of the research at NASA LaRC is on CFRP materials and the detection of minute amounts of silicone by monitoring the Si peak from the laser induced plasma. Relevant data are provided to support the feasibility of LIBS as a rapid means to enable quality control of CFRP surfaces prior to adhesive bonding. These results have established the fundamentals for the conception and current implementation of a closed loop control system based on laser technology [12].

Control (as fabricated) and purposely silicone contaminated surfaces were investigated to determine the effect of the residual contaminant on the bond performance [2]. A 355 nm, 10 ps laser system was used for LIBS and laser treatment (LT). Microjoule LIBS was used to detect

silicone contamination before and after LT. Figure 3 shows the Si/C ratio as a function of the silicone areal density deposited on a surface prior to LT.

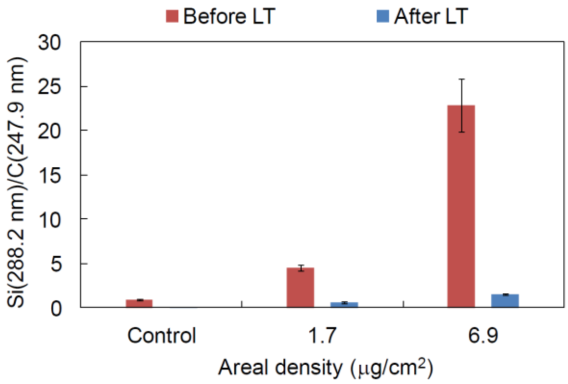

Figure 3. Si/C ratios from the LIBS measurements before and after laser surface treatment using picosecond pulses [2].

Surface characterization using LIBS (before and after laser treatment) with 355 nm, 10 ps pulses was performed on CFRP panels for detection of ultra-thin silicone contamination layers from 0.15 μg/cm^2 to 2 μg/cm^2 (thickness of 1.6 nm to 20 nm) [8]. LIBS was performed using 15 μJ pulses with a single shot on a fresh surface to maximize surface sensitivity. Optimization of laser parameters was studied to decrease the material ablation for LIBS inspection. Time-resolved analysis was conducted to determine optimal plasma conditions to detect Si. The LIBS instrument was sensitive enough to detect residual Si after laser surface treatment.

Surface sensitivity and the LIBS limit of detection (LOD) were investigated for the detection of silicone at various concentrations on CFRP surfaces [9]. XPS and LIBS analyses were performed on identical samples. XPS data were obtained from two different laboratories, BTG Labs (Cincinnati, OH) and NASA LaRC (Hampton, VA). For quantitative analysis, analytical calibration curves were constructed (Figure 4). From the calibration curves, it was possible to determine the detection limits of LIBS, which were below 0.6 at.%. These results demonstrated the advantages of LIBS over XPS for rapid detection of minute quantities of silicone contaminants, with high surface sensitivity and no special atmosphere or sample preparation.

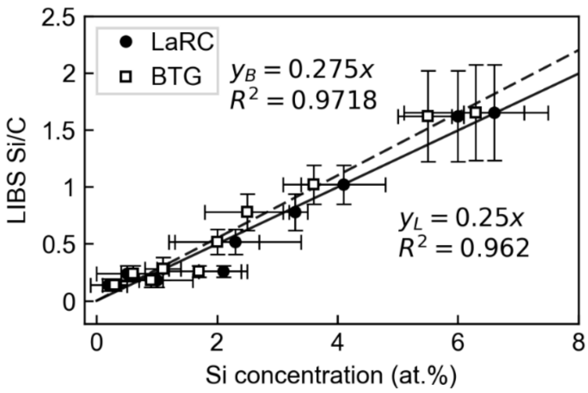

Figure 4. Analytical calibration curves with the Si/C ratio from LIBS and the Si concentration from XPS. The linear fits y_L (solid line) and y_B (dashed line) correspond to LaRC and BTG, respectively. (Reprinted from [9] with permission of SAGE Publishing).

5.1 Surface mapping

LIBS data can be collected at specific locations, and each location can provide a better understanding of the surface condition in that region. In Figure 5, the yellow dots represent the locations where LIBS was measured. The LIBS Si/C ratio from those locations can be correlated to the surface morphology or failure modes observed in failed bonded test specimens. The numbers in parentheses represent the Si/C ratios determined before (white) and after (orange) laser ablation at 200 mW, 355 nm, and a pulse width of 10 ps.

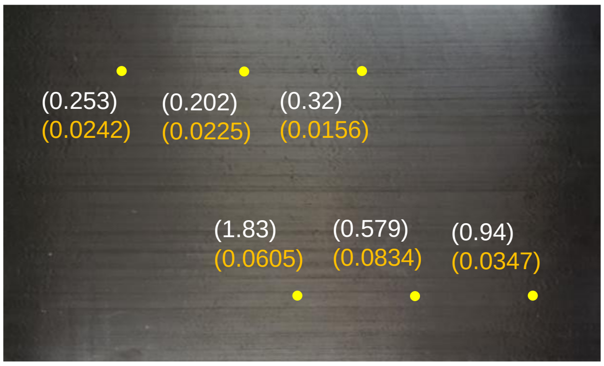

Figure 5. Surface mapping of a composite panel showing the LIBS Si/C ratios before (white) and after (orange) laser ablation.

Another example of surface mapping is when laser surface treatment and LIBS are conducted simultaneously to treat a specific area. In this case, four linearly arranged collimators continuously collected the plasma emissions as the laser was ablating the surface. Ten parallel lines (3.81 cm) were ablated at 200 kHz, 2 W average power (10 µJ pulse energy), and 254 cm/s scan speed, separated by 12.7 µm to produce a surface map using the Si/C ratios. Figure 6 shows the LIBS spectra for one line obtained from the first and second passes on the same location. After the first pass, there are strong Si peaks (between 250 nm and 255 nm, and at 288.2 nm). After the second pass, the Si peaks were not detected, indicating the removal of the silicone contaminant from the CFRP surface. The ablative overlap produced at 200 kHz pulse rate and 254 cm/s was enough for 10 µJ pulses to remove the silicone contaminant after two passes.

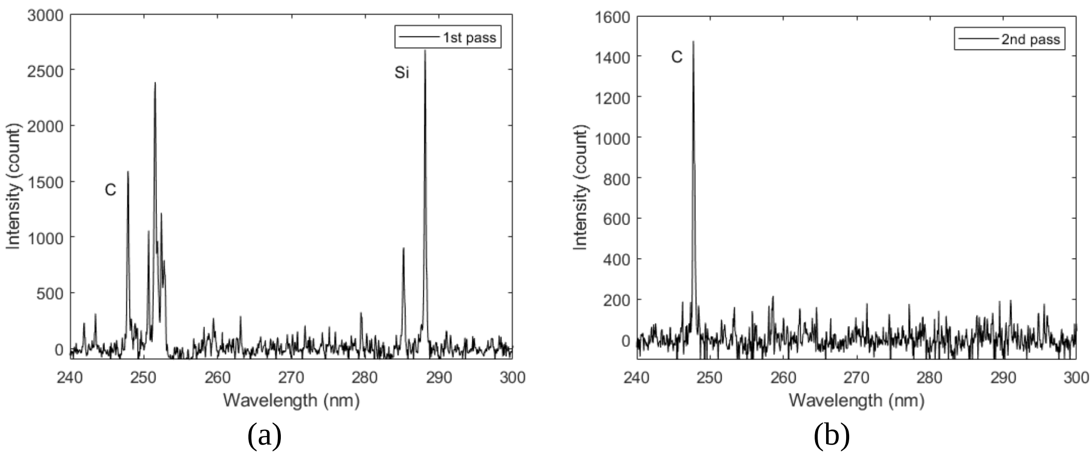

Figure 6. LIBS spectra of one ablated line after (a) the first pass and (b) the second pass. After the second pass, the Si peaks were not present and only the C peak was detected.

Figure 7 shows the 2D surface maps using the calculated Si/C ratios from the LIBS measurements from the ten lines. Non-uniform distribution of silicone concentration was detected after the first ablation pass, as seen in Figure 7a. After the second pass on the same area, the silicone concentration was significantly reduced (Figure 7b).

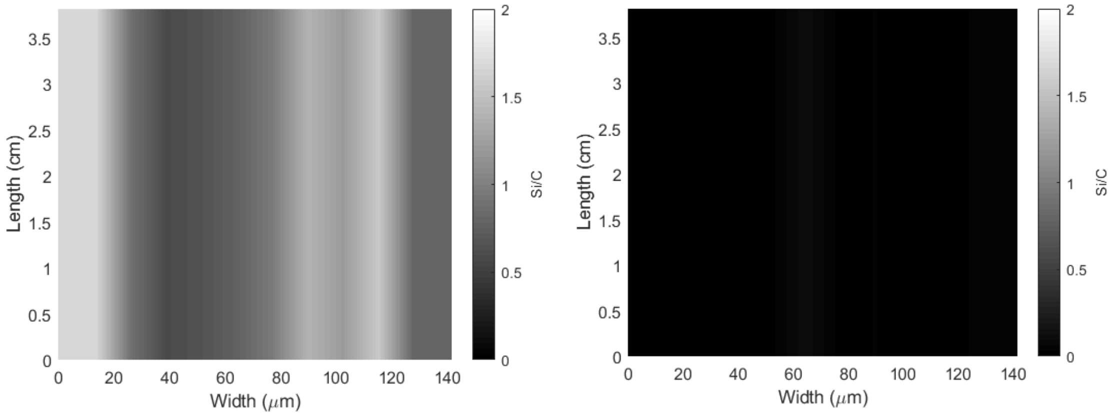

Figure 7. Surface mapping of an ablated region of 3.81 cm x 141.4 µm. Silicone contamination was observed for (a) the first ablation pass but was significantly reduced in (b) the second pass.

5.2 Mechanical testing

PEEK thermoplastic panels were laser treated and co-bonded with FM309-1 (Solvay) and AF-555 (3M Scotch-Weld) adhesives to IM7/8552 (Hexcel) thermoset prepreg to prepare double cantilever beam (DCB) samples (Figure 8). LIBS inspection was completed pre and post laser treatment and indicated that silicone contamination levels were reduced sufficiently to proceed with bonding. The specimens were configured by bonding one end of the panel with AF-555 and the opposite end with FM309-1. Precracks (fluorinated ethylene propylene (FEP) film, 12.7 µm thick) were inserted at both ends of the laminates so that each specimen could be tested from each end to double the number of tests conducted on each bonded panel. The laser treatment process was based on the legacy laser treatment parameters developed at NASA LaRC (Table 1). Figure 9 shows the fracture surfaces after DCB testing. The fracture surfaces show predominantly uniform cohesive failure mode, with some fiber tear on the AF-555 end. Cohesive failure in the adhesive indicates excellent bond performance of the surface treatment. At the time this report was written, no results were available to compare the LIBS-compatible laser surface treatment with the legacy process. Still, this result confirms that laser treatment and reduction of the Si/C ratio as measured by LIBS correlates with high performance bonding.

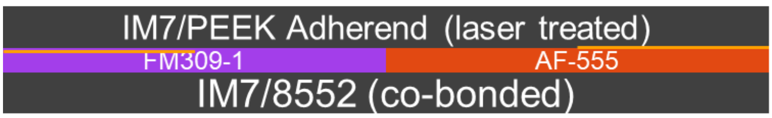

Figure 8. Sample configuration for DCB testing of laser treated IM7/PEEK. The orange line at the adhesive-IM7/PEEK interface shows the location of precrack (FEP film, 12.7 µm thick). Drawing not to scale.

Table 1. Laser treatment parameters based on legacy surface treatment process. Each laminate surface was treated with one laser pass. The laser wavelength was 355 nm and the pulse width was nominally 10 ps.

	Power (mW)	Frequency (kHz)	Scan speed (cm/s)	Line pitch (µm)
Panel 1	380	325	20	20.3
Panel 2	380	325	30	20.3

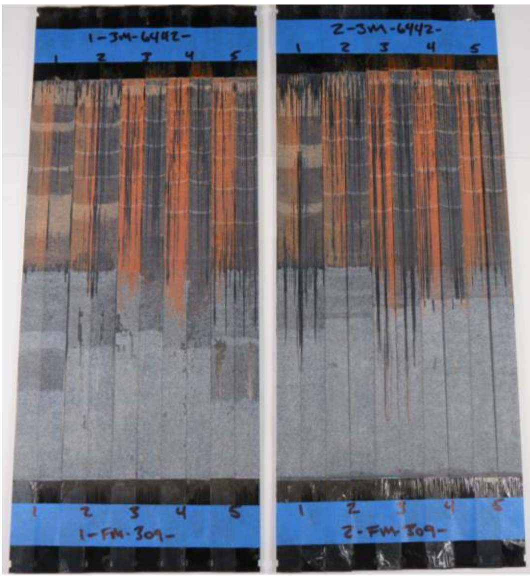

Figure 9. Fracture surfaces for two panels, previously laser treated, showing uniform cohesive failure mode. Panel 1 is left, Panel 2 is right (see Table 1 for details).

6. Summary

Laser surface treatment has been investigated at NASA LaRC to remove ultralow levels of surface contamination, chemically activate the surface, and increase surface area prior to adhesive bonding and coating processes. Silicones are ubiquitous in the fabrication process of CFRP substrates and, even at low concentrations, can significantly diminish adhesive bond performance. The LIBS system has been utilized and tuned as a surface quality control tool for the detection of silicone contaminants and was demonstrated to be an adequate and robust technique that can be integrated for in-line control of a bonding process.

The LIBS instrument developed at NASA LaRC was shown to be surface sensitive comparable to XPS. Extensive research has been conducted at NASA LaRC to prove the reliability of LIBS for the detection of ultralow levels of silicone species on CFRP surfaces prior to adhesive bonding.

The closed loop system described in this work is an advancement of the current apparatus to enhance the utility and speed of the LIBS and laser treatment processes. By integrating both systems, the LIBS and laser treatment can be automated to improve the repeatability and surface inspection times, and therefore, it can reduce the certification times of adhesive bonded structures. Preliminary results indicate that LIBS inspection and laser treatment can be conducted simultaneously to achieve high quality, reliable adhesive bonds.

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7. References

1. Palmieri F, Belcher M, Wohl C, Blohowiak K, Connell J. Laser ablation surface preparation for adhesive bonding of carbon fiber reinforced epoxy composites. Int. J. Adhes. Adhes. 2016;68:95-101.
2. Palmieri F, Ledesma R, Fulton T, Arthur A, Eldridge K, Thibeault S, Lin Y, Wohl C, Connell J. Picosecond pulsed laser ablation for the surface preparation of epoxy composites. SAMPE Seattle; 2017 May 22-25.
3. Ledesma R, Palmieri F, Connell J. Laser induced breakdown spectroscopy of polymer matrix composites for real-time analysis of trace surface contaminants: A review. *Int. J. Adhes. Adhes.* 2020;98.
4. Palmieri F, Watson K, Morales G, Williams T, Hicks R, Wohl C, Hopkins J, Connell J. Laser ablative surface treatment for enhanced bonding of Ti-6Al-4V alloy. ACS Appl. Mater. Interfaces. 2013;5:1254-1261.
5. Pou-Alvarez P, Riveiro A, Novoa XR, Fernandez-Arias M, del Val J, Comesaña R, et al. Nanosecond, picosecond and femtosecond laser surface treatment of magnesium alloy: role of pulse length. Surf. Coat. Technol. 2021;427:127802.
6. Srinivasan R, Braren B. Ultraviolet laser ablation of organic polymers. Chem. Rev. 1989;89:1303-1316.
7. Gedvilas M, Raciukaitis G. Investigation of UV picosecond laser ablation of polymers. Proc. SPIE, Workshop on Laser Applications in Europe. 2005;6157:61570T.
8. Ledesma R, Palmieri F, Connell J, Yost W, Fitz-Gerald J. Surface characterization of carbon fiber reinforced polymers by picosecond laser induced breakdown spectroscopy. Spectrochim. Acta, Part B. 2018;140:5-12.
9. Ledesma R, Palmieri F, Campbell B, Yost W, Fitz-Gerald J, Dillingham G, Connell J. Correlation of trace silicone contamination analyses on epoxy composites using X-ray photoelectron spectroscopy (XPS) and laser-induced breakdown spectroscopy (LIBS). Appl. Spectrosc. 2019;73:229-235.
10. Palmieri F, Ledesma R, Cataldo D, Lin Y, Wohl C, Gupta M, Connell J. Controlled contamination of epoxy composites with PDMS and removal by laser ablation. SAMPE Long Beach; 2016 May 23-26.
11. Palmieri F, Ledesma R, Dennie J, Kramer T, Lin Y, Hopkins J, Wohl C, Connell J. Optimized surface treatment of aerospace composites using a picosecond laser. Composites, Part B. 2019;175.
12. Connell J, Palmieri F, Yost W, Hopkins J, Ledesma R. Laser surface treatment and spectroscopic analysis system. U.S. Patent Application Publication, US 2019/0033231; 2019 Jan. 31.

